Synthesis and Characterization of Poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] Copolymers

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ABSTRACT: Poly(trimethylsilylpropyne) copolymers with bromobutyl side chains were synthesized from 1-trimethylsilyl-1-propyne and 1-(4-bromobutyldimethylsilyl)-1-propyne using a $TaCl_5/Ph_3Bi$ catalyst system in toluene. After polymerization, azide groups were introduced into the polymers by phase transfer catalysis to yield poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] copolymers. Results from thermal analyses, elemental analyses, and IR spectroscopy confirm that the azide content in the copolymers matches the original comonomer feed ratios. Films of the copolymers were thermally cross-linked in vacuo, with the rate of azide decomposition monitored by the loss of the azide absorption band in the IR. For a copolymer with 15 mol % azide content, an activation energy of 130 kJ/mol was calculated from IR data collected over the azide decomposition temperature range. For the copolymer with the highest azide content (20 mol %), DSC measurements give −1.2 kJ/g for the enthalpy of azide decomposition. Swelling experiments performed on the cross-linked films indicate that a relatively low cross-link density (∼5%) is required to render membranes dimensionally stable in good solvents for the polymer.

Introduction

Organic azides are particularly useful intermediates in synthetic chemistry because they are readily introduced into molecules and can be transformed into a variety of functional groups such as amines, azo compounds, and isocyanates. In addition, organic azides are key intermediates in carbohydrate chemistry[1] and for the preparation of heterocyclic compounds.[2,3] Recently, new applications have been developed that exploit the reactivity of the nitrenes that are generated when azides are decomposed thermally or photochemically. Because of the highly energetic decomposition of azides, azide-containing materials such as glycidyl azide polymers (GAP)[4−6] and bis-azide methyloxetane polymers (BAMO)[7,8] have been explored as binder materials that increase the burning rates of propellants. Organic azides also can be used to cross-link or modify the surface of materials, yielding materials with vastly different properties. For example, azide-based surface modifications have been used to improve the biocompatibility of prosthetic implants, which are often rejected by the body due to poor hemocompatibility.[9−12] Encapsulation of platelet activation inhibitors on polyurethane surfaces by azide cross-linking leads to new materials with improved biocompatibility. The azide functionality also is a key part of photoaffinity labeling schemes that study transient protein/protein interactions.[13−16] In these experiments, azide-labeled protein strands are cross-linked to receptor proteins, enabling identification of the receptor site.

Organic azides are widely used for cross-linking polymers.[17−23] Azides have three advantages as cross-linking agents. They are easily synthesized, most commonly via S_N2 substitution chemistry using sodium azide and a phase transfer agent, but preparation from a large number of other functional groups has also been reported.[1] Azides are latent cross-linking agents and can be independently activated by thermal, photochemical, or chemical means when cross-linking is desired, increasing the flexibility of material processing. Finally, azide functional groups decompose to nitrogen gas and reactive nitrenes that undergo insertion reactions.[24] Thus, no low molecular weight byproducts are formed that could contaminate the material.

Azide-based cross-linking is particularly attractive for the stabilization of membranes used for gas and liquid separations. Membrane swelling by components of a mixture can decrease the efficiency of separations, and without some cross-linking to control the dimensional changes, the membrane will fail. In a recent publication we explored the preparation of cross-linked poly[1-trimethylsilyl-1-propyne] (PTMSP) membranes using bis(aryl azide)s.[23] Since it was first synthesized,[25] PTMSP has been a material of particular interest for gas separations because its high free volume results in oxygen permeability roughly 10 times that of poly(dimethylsiloxane), the polymer typically used as a benchmark for high permeability.[26] Unfortunately, a major drawback of PTMSP is that the permeability declines with time,[27] an effect that has been attributed to aging (densification) or contamination. Cross-linking PTMSP membranes with aryl azides stabilized their permeability and rendered the membranes insoluble. However, one limitation of the bis(aryl azide) cross-linking approach is that the azides phase separate from PTMSP at relatively low concentrations (≈5 wt %), and thus the cross-link density is limited by the solubility of the cross-linking agents in the polymer matrix. Increased cross-link densities are needed for better control of the pore size in PTMSP and to minimize polymer swelling in liquid separations.

Higher cross-link densities could be obtained by preparing bis(azide)s that are more compatible with PTMSP or by directly attaching azides to the polymer backbone. A disadvantage of the former approach is that the added azides occupy much of the free volume in the

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polymer, leading to a large drop in permeability.[23] Direct attachment of azides to the polymer eliminates the phase separation problem and minimizes the size of the cross-linking agent. The structure of PTMSP suggests three strategies for incorporating azides into PTMSP: reactions involving the main chain double bonds, substitution reactions at allylic methyl sites, or copolymerization with an acetylenic comonomer having either an azide group or a suitable azide precursor. In this report, we explore strategies for the direct attachment of azides to the PTMSP framework and characterize the cross-linking behavior of the resulting polymers.

Experimental Section

Materials. Tetrahydrofuran (THF) and toluene were purified by distillation from calcium hydride followed by a second distillation from sodium/benzophenone ketyl. Unless otherwise specified, all other ACS reagent grade starting materials and solvents were used as received from commercial suppliers without further purification.

Characterization. Proton nuclear resonance (^{1}H NMR) spectra were measured using a Varian Gemini-300 spectrometer at 300 MHz. All samples were run at room temperature in $CDCl_3$. Chemical shifts were calibrated using residual $CHCl_3$ and are reported in ppm (δ) relative to tetramethylsilane. Infrared spectra of polymers were obtained under nitrogen at room temperature on a Nicolet Magna-IR 550 Fourier transform IR spectrometer. IR measurements of samples before and after thermal treatment were carried out on films cast on NaCl disks. A Hitachi U-4001 UV−vis spectrometer was used to obtain the UV−vis spectra of cyclohexane solutions of the polymers. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 20μ mixed A column and a Waters R401 differential refractometer detector at room temperature with THF as eluting solvent at a flow rate 1 mL/min. Monodisperse polystyrene standards were used to calibrate the molecular weights. The concentration of the polymer solutions used for GPC measurements was 1 mg/mL. Differential scanning calorimetry (DSC) data were obtained under a He environment using a Perkin-Elmer DSC 7 instrument at a heating rate of 10 °C/min. The DSC 7 temperature was calibrated with an indium standard. Thermogravimetric analyses (TGA) were performed under nitrogen and air atmospheres at a heating rate of 10 °C/min on a Perkin-Elmer TGA 7 instrument. Elemental analyses were performed at the Microanalysis Laboratory at the University of Illinois, Urbana−Champaign, using a CE440 carbon, hydrogen, nitrogen analyzer (Exeter Analytical, Inc.) and conventional Br analysis (titration).

Poly[1-trimethylsilyl-1-propyne]. PTMSP was prepared following a literature procedure.[28−30] A solution of 1-trimethylsilyl-1-propyne (0.64 g, 5.7 mmol) in dry toluene (10 mL) was degassed by three freeze/pump/thaw cycles. The monomer solution was then added via cannula to a mixture of tantalum pentachloride (120 mg, 0.34 mmol) and triphenylbismuth (150 mg, 0.34 mmol). The reaction mixture was heated to 80 °C and stirred for 16 h. The resulting gel-like product was dissolved by adding more toluene, centrifuged to remove catalyst residues, and precipitated by slow addition into an excess of methanol with rapid stirring. Redissolving in toluene and reprecipitating into methanol yielded 0.51 g (80%) of poly[1-trimethylsilyl-1-propyne]. GPC: $M_n = 750\,000$. $M_w/M_n = 2.3$. ^{1}H NMR: δ 0.25 (br, 9H), 1.75 (br, 3H).

Allylic Bromination of PTMSP. Partially brominated PTMSP (50%) was prepared following the literature procedure[31] by reacting PTMSP (1.0 g) with *N*-bromosuccinimide (0.79 g, 4.5 mmol) in refluxing CCl_4 (100 mL) in the presence of benzoyl peroxide (100 mg). Conversion to the brominated product was determined by monitoring the formation of a signal at 2.2 ppm in the ^{1}H NMR and an absorption band at 1219 cm^{-1} in the IR spectra due to the introduction of $-CH_2$-Br. The yield was nearly quantitative.

Azidization of Brominated PTMSP. Brominated PTMSP (0.50 g, 2.2 mmol Br) was dissolved in either 25 mL of benzene or THF under a nitrogen atmosphere. The phase transfer reagent (18-crown-6 ether, 29 mg, 0.11 mmol) and NaN_3 (0.58 g, 8.9 mmol) or LiN_3 (0.44 g, 8.9 mmol) were added at the desired temperature (50 °C for THF and 60 °C for benzene). The reaction mixture was sampled at different times and precipitated into methanol, and the conversion was determined by ^{1}H NMR and IR spectroscopy. For reactions using $ZnCl_2$, the same procedure was used except that $ZnCl_2$ (0.18 g, 0.73 mmol) and pyridine (2.2 mmol) were used in place of the phase transfer reagent.

4-Bromo-1-butene (2). 4-Bromo-1-butene was prepared according to the literature procedure[32] in 37% yield (21 g); bp 98−100 °C (lit.[32] 98−100 °C). ^{1}H NMR: δ 2.7 (m, 2H), 3.3 (t, 2H), 5.1 (m, 1H), 5.8 (m, 2H).

4-Bromobutyldimethylchlorosilane (3). Compound **3** was prepared following the procedure of Kunzler and Percec[33] in 85% yield (17.9 g); bp 90−95 °C/23 mmHg (lit.[33] 92−95 °C/5 mmHg). ^{1}H NMR: δ 0.4 (s, 6H), 0.8 (t, 2H), 1.5 (m, 2H), 1.9 (m, 2H), 3.4 (t, 2H).

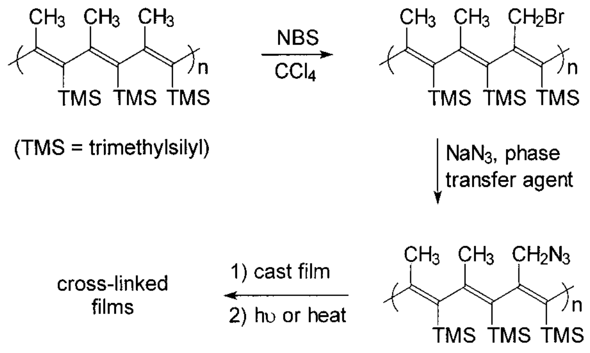
1-(4-Bromobutyldimethylsilyl)-1-propyne (4). A solution of propynyllithium was prepared by the dropwise addition of *n*-BuLi (2.5 M in hexanes, 12 mL) to a cold propyne−ether solution obtained by bubbling propyne gas through cold diethyl ether (−78 °C). To the solution of propynyllithium was added 4-bromobutyldimethylchlorosilane (6.7 g, 29 mmol) dropwise at 0 °C. The reaction mixture then was stirred overnight at room temperature and then poured into 400 mL of ice water. The ether layer was collected and washed with distilled water, dried over $MgSO_4$, and filtered, and the solvent was removed by rotoevaporation. The remaining oil was purified by vacuum distillation at 59−65 °C/3 mmHg to yield 4.6 g (68%) of 1-(4-bromobutyldimethylsilyl)-1-propyne (lit.[33] 70−75 °C/15 mmHg). ^{1}H NMR: δ 0.15 (s, 6H), 0.6 (t, 2H), 1.5 (m, 2H), 1.85 (s, 3H), 1.9 (m, 2H), 3.4 (t, 2H).

Poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)] (5a−5g). The following procedure, illustrated for the synthesis of the copolymer containing 20 mol % of the 1-(4-bromobutyldimethylsilyl)-1-propyne comonomer, was used to prepare all of the copolymers. A mixture of 1-trimethylsilyl-1-propyne (5.23 g, 0.047 mol) and 1-(4-bromobutyldimethylsilyl)-1-propyne (2.72 g, 0.012 mol) was dissolved in dry toluene (100 mL) and degassed by three freeze/pump/thaw cycles. The monomer solution was then added via cannula to a mixture of tantalum pentachloride (0.835 g, 2.33 mmol) and triphenylbismuth (1.025 g, 2.33 mmol). The reaction mixture was heated to 80 °C and stirred for 16 h. The resulting gel-like product was diluted with toluene, centrifuged to remove residual catalyst, and precipitated by slow addition into an excess of methanol with rapid stirring. Redissolving in toluene and reprecipitating into methanol yielded 6.54 g (83%) of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)]. GPC: $M_n = 432\,000$. $M_w/M_n = 2.4$. ^{1}H NMR: δ 0.2 (br), 1.6 (br), 1.8 (br), 3.4 (br).

Poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] (6a−6g). Sodium azide (0.65 g, 10 mmol) and a catalytic amount of tetrabutylammonium hydrogen sulfate (TBAH, 100 mg) were added to a stirred solution of 1.0 g of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)] (**5g**) in 100 mL of THF. The reaction mixture was stirred for 120 h at 60 °C. The resulting polymer was dissolved in additional THF and centrifuged to remove most of the catalyst and other undissolved solids. The cloudy polymer solution was washed with water to remove salts not removed by centrifugation. The resulting clear solution was precipitated into methanol, filtered, redissolved in THF, and again precipitated in methanol. The collected polymer was vacuum-dried at 50 °C overnight to obtain 0.90 g (90%) of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)]. GPC: $M_n = 410\,000$, $M_w/M_n = 2.6$. ^{1}H NMR: δ 0.2 (br), 1.6 (br), 1.8 (br), 3.25 (br).

Film Casting and Cross-Linking. Viscous casting solutions were obtained by dissolving the copolymer (200 mg) in

Scheme 1



toluene (10 mL). Polymer films were prepared by pouring the casting solutions onto a flat glass plate and drying for 48 h. The films were then completely dried in a vacuum oven at 50 °C overnight. Thermal cross-linking of the resulting free-standing copolymer films was achieved by heating the samples in a vacuum oven at 250 °C for 3 h.

Swelling Experiments. Cross-linked copolymer films were cut into 2 cm × 2 cm pieces, weighed, and immersed in solvents with solubility parameters (δ) ranging from 14×10^3 to 20×10^3 $(\mathrm{J/m^3})^{1/2}$. After 24 h, the films were removed from the solvent, blotted dry, weighed, and placed back into the solvent. This procedure was repeated until the samples reached a constant weight. The reported swelling values are the average of three individual film measurements.

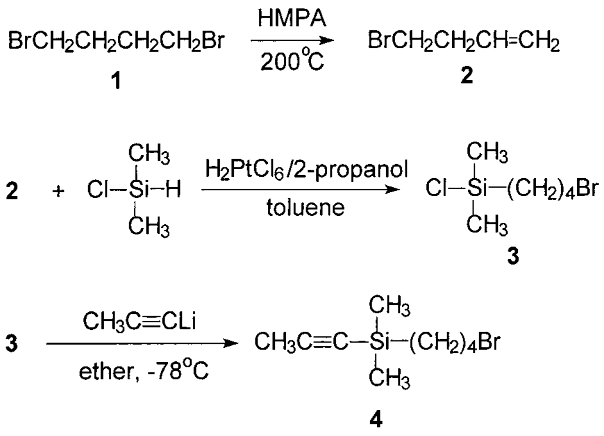
Results

Incorporation of Azides at Allylic Sites. Despite numerous attempts and the use of various reaction conditions, it has been shown that the double bonds of the PTMSP backbone are unreactive.[33] Low reactivity for these double bonds is not unexpected because of the severe steric effects caused by the methyl and trimethylsilyl side groups. Direct attachment of azides to the allylic methyl groups of PTMSP is an attractive strategy for accessing PTMSP polymers with high azide contents and high degrees of cross-linking because the small size of the azide group should result in minimal structural changes compared the parent polymer. As shown in Scheme 1, brominated PTMSP was prepared using standard free-radical conditions,[31,34] and various methods were examined for nucleophilic displacement of the bromide by azide. Allyl azides are easily prepared from allyl bromides by reaction with NaN_3 or trimethylsilyl azide,[35] and similar methods have been used to partially convert halogen-containing polymers such as poly(vinyl chloride)[36−38] and poly(epichlorohydrin)[39] to polymeric azides. However, we found that substitution chemistry at the allylic methyl group in PTMSP is highly hindered. Both IR and ^1H NMR spectroscopy showed no evidence of incorporation of azide in the polymer.

Since S_N2 chemistry failed, we followed the procedure of Ravindranath et al.[40] and used Lewis acids to form allylic carbocations that could be trapped by the azide anions. The product from the azidization reaction of 50% brominated PTMSP showed a small peak at 2100 cm^{-1} in the IR spectra, indicating the presence of the $-N_3$ group, but a strong $BrCH_2-$ vibrational band at 1219 cm^{-1} was still evident. Proton NMR also indicated only partial introduction of the azide. Our best results show only limited success, with less than 5% conversion to the azido derivatives after 5 days.

Incomplete conversion to the azide is a serious problem since brominated PTMSP degrades rapidly in the presence of UV light and oxygen.[34] Before these polymers can be cross-linked into insoluble films, the remaining bromide must be removed while retaining the azides. We tried to replace the remaining bromine with hydrogen by treating the azido derivatives with Bu_3SnH/AIBN. After reacting in toluene at 75 °C for 2 h, IR spectra showed the disappearance of both the $-N_3$ and the $BrCH_2-$ bands, indicating that the reaction was not selective and that hydride replaced the bromide and reduced the azide group.

Scheme 2



We also examined anionic methods for substitution at the methyl group. For example, brominated PTMSP treated with either BuLi or Li metal generated the allylic anion, but gelation was observed in these reactions and the resulting polymers became insoluble and unprocessable. Presumably, slow formation of the anion allowed the coupling of anions with residual allyl bromides to give a cross-linked network.

Incorporation of Azides via Copolymerization. Because steric hindrance at the allylic methyl group resulted in only partial conversion of the allylic bromide to the azide, we decided to increase the reactivity of the halide by moving it away from the polymer backbone. While the tether could be connected to either the allylic methyl or trimethylsilyl group of the monomer, attachment through the trimethylsilyl group should have the least effect on the polymerization rate since the site of the substitution is farther from the triple bond. Following the approach of Kunzler and Percec,[33] we prepared copolymers of 1-trimethylsilyl-1-propyne and 1-(4-bromobutyldimethylsilyl)-1-propyne. Azide groups can be introduced into these copolymers by simple nucleophilic displacement reactions. Because monomers containing azides are unlikely to survive the polymerization conditions, we did not explore the direct polymerization of an azide-containing monomer.

The comonomer, prepared by the route outlined in Scheme 2, was copolymerized with 1-trimethylsilyl-1-propyne (Scheme 3) to give a series of copolymers that contain 2−20 mol % of 1-(4-bromobutyldimethylsilyl)-1-propyne. GPC measurements showed that the molecular weights of the copolymers were similar to those of PTMSP, ranging from 4×10^5 to 5×10^5 with a polydispersity of 2.5. Treatment of the copolymer with sodium azide and a phase transfer agent smoothly converted the bromobutyl side chain to the corresponding azide. The reaction was sampled at different times and analyzed by ^1H NMR and FTIR spectroscopy to determine the conversion. In the IR spectra, the intensity of the band at 1219 cm^{-1} decreased (CH_2 wagging, CH_2Br group), and a new band grew in at 2100 cm^{-1}

Scheme 3

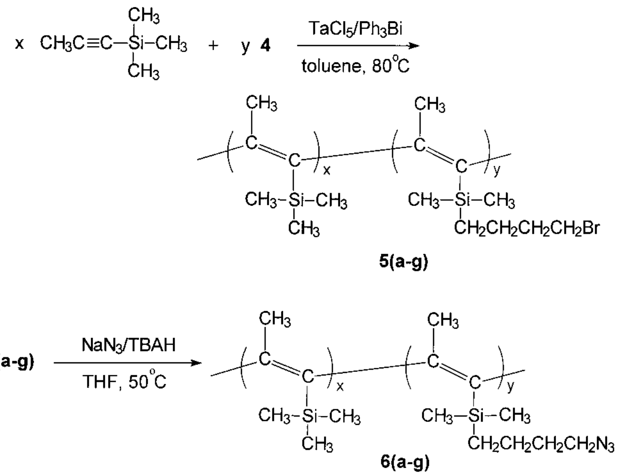


Table 1. Elemental Analyses of Poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] Copolymers

	5		10		20	
	theor	expt	theor	expt	theor	expt
	Theoretical N_3 (mol %)[a]					
C %	63.46	63.26	62.76	62.80	61.52	60.61
H %	10.61	10.02	10.45	10.25	10.17	7.68
N %	1.80	1.36	3.49	2.71	6.52	5.45
Si %	24.13	*b*	23.30	27.79	21.79	24.95
	Experimental N_3 (mol %)[c,d]					
	3.8		7.8		17.0	

[a] Calculated by assuming 100% conversion from poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)]. [b] Not analyzed. [c] Calculated from elemental analysis results. [d] Br was not detected using titration method.

that corresponds to the $-N_3$ group[41] in poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)]. Corresponding changes were seen in the ^{1}H NMR data. The peak at 3.4 ppm from the $-CH_2Br$ segment in poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)] decreased as a new resonance at 3.25 ppm for $-CH_2N_3$ in poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] increased. The peak at 3.4 ppm in the ^{1}H NMR spectra and the absorption band at 1219 cm^{-1} in the IR spectra both decreased to baseline, demonstrating that complete displacement of the bromide was achieved after 5 days.

Polymer Characterization. Elemental analyses (Table 1) of the copolymers showed no bromine detectable by titration, confirming the high degrees of bromide to azide conversion indicated in the ^{1}H NMR and IR data. The absolute azide content in the copolymers can also be calculated from the experimental C/N ratios. We found that the azide contents of copolymers calculated from elemental analyses data result in ≈20% lower values than expected. The deviations from the expected values may be due to PTMSP's tendency to form refractory oxides in oxidizing environments.[42]

Shown in Figure 1 are the IR spectra of the series of copolymers with increasing azide contents. The spectra are normalized relative to the intensity of the C=C absorption (1600 cm^{-1}) of the polymer backbone. The most prominent feature in the spectra is the increase in the intensity of the absorption band for the alkyl azide at 2100 cm^{-1}. This increase is mirrored by a growth in the intensity of the aliphatic C−H stretching bands (2800−3000 cm^{-1}) caused by the increase in the concentration of alkyl side chains in the higher azide content copolymers. When the integrated intensity of the azide absorption bands is plotted versus the theoretical azide calculated from the comonomer feed ratios (Figure 2), we obtain a linear relationship indicating that the overall composition of the samples are comparable to the initial monomer ratios.

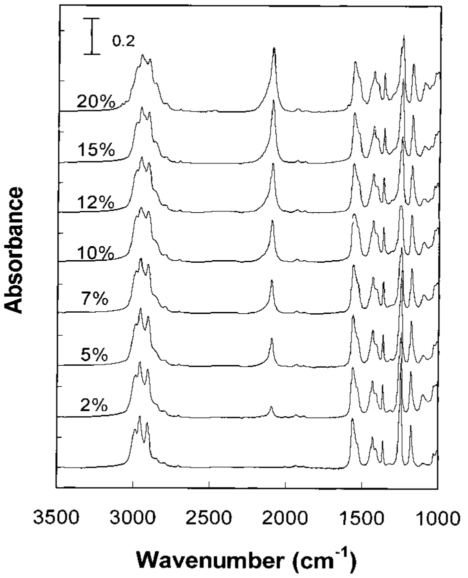


Figure 1. FTIR spectra of PTMSP and copolymers **6a**−**6g**. The numbers next to each curve indicate the azide content (*y*) in the copolymer.

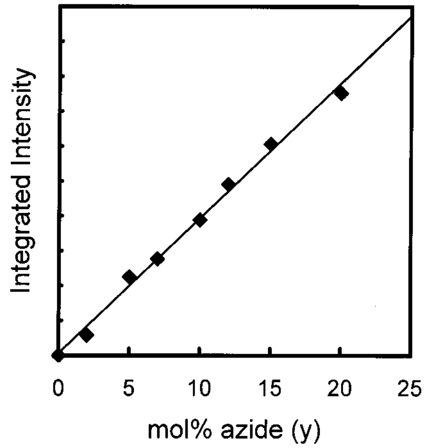


Figure 2. Comparison of the integrated azide absorption bands in the IR (2100 cm^{-1}) with the azide content in copolymers **6a**−**6g** calculated from the comonomer feed ratios. The integrated peak areas of the 2100 cm^{-1} band were normalized for film thickness and are plotted in arbitrary units.

UV−vis spectra of cyclohexane solutions of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] show no absorption above 300 nm. Absorption bands of alkyl azides[41] typically occur at λ_{max} = 287 nm (ϵ = 25) and λ_{max} = 216 nm (ϵ = 500), but the strong C=C absorption of the polymer backbone masks the azide absorption in these samples. Like PTMSP, the azide-containing copolymers are snow-white solids after precipitation into methanol and form clear, colorless films when cast from solvents such as THF or toluene.

Thermogravimetric analyses (Figure 3) of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsi-

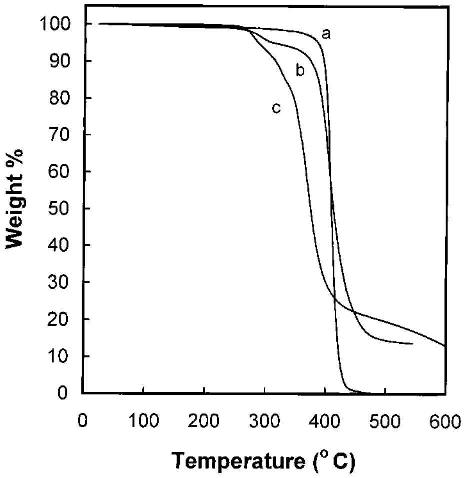


Figure 3. TGA of (a) PTMSP under nitrogen, (b) copolymer **6g** under nitrogen, and (c) copolymer **6g** under air (heating rate of 10 °C/min).

lyl)-1-propyne)] under nitrogen show the onset of a weight loss at 225 °C due to the decomposition of the azide groups and the release of nitrogen from the polymer. Depending upon the density of the original sample, the subsequent cross-linking reactions result in a 10−20% char yield at 600 °C. In contrast, PTMSP is thermally stable to 350 °C and then rapidly decomposes to monomer, yielding no residue. When run in air, the copolymers again evolve nitrogen at 225 °C, but the resulting products are less stable and decompose more rapidly. The weight loss due to evolution of nitrogen could, in principle, be used to quantitate the N_3 contents in the copolymers. However, the weight loss from nitrogen evolution partially overlaps with a weight loss associated with a slow degradation of the polymer, and consistent values could not be obtained.

DSC measurements on poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] copolymers show no thermal transitions below the azide decomposition temperature (<225 °C), indicating that, like PTMSP,[43] the copolymers do not exhibit a glass transition. We interpret the similarity of the PTMSP and copolymer DSC scans as evidence that the added side chains did not drastically alter the physical properties of the PTMSP backbone. The exothermic transition for azide decomposition is centered at 270 °C in the DSC thermograms and can be quantitatively related to the azide content in the copolymers. Figure 4 shows that the enthalpy change associated with the exotherm is linearly related to the azide content in the copolymers calculated from the original comonomer feed ratios. This result can be anticipated from the data of Figure 2, which verified that the monomer feed ratio and the polymer composition are identical. The plot also yields a positive *y*-intercept. As the data are all offset by a fixed amount relative to the origin, we believe the nonzero intercept may reflect some thermally induced changes in PTMSP. Isothermal aging of PTMSP at 250 °C for several hours shows a decrease in molecular weight loss, and thus it is reasonable to ascribe the nonzero intercept to a small amount of polymer degradation.

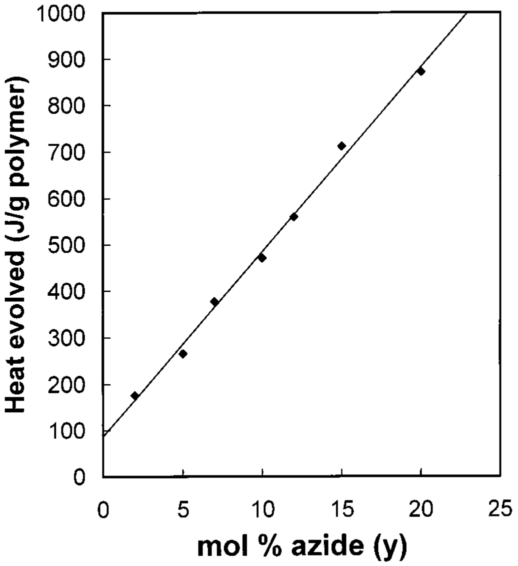


Figure 4. Heat evolved during thermal decomposition of azide copolymers **6a**−**6g** measured by DSC (heating rate of 10 °C/min under He).

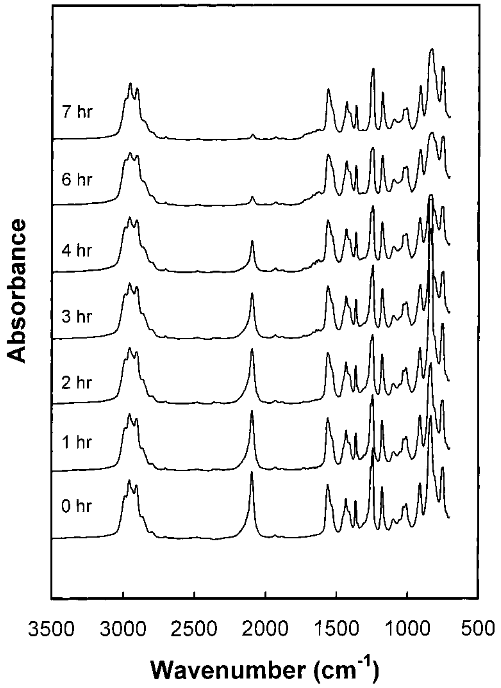


Figure 5. FTIR spectra showing the thermal decomposition of copolymer **6f** at 225 °C under vacuum.

Thermal Cross-Linking of Copolymer Films. We studied the thermal decomposition of the azide-containing copolymers from 225 to 275 °C, the temperature range that corresponds to the exotherm measured in the DSC curves and the nitrogen weight loss seen in the TGA thermograms (Figure 3). As shown in Figure 5 for thermal decomposition at 225 °C, the rate of the reaction can be followed by monitoring the decrease in the intensity of the N_3 absorption at 2100 cm^{-1} in the IR. We assumed that the azide concentrations in the films are proportional to the integrated absorption intensities in the normalized IR spectra. Using eq 1,

$$-\ln\left(\frac{[N_3]_t}{[N_3]_0}\right) = k_d t \qquad (1)$$

where $[N_3]_0$ and $[N_3]_t$ are the azide concentrations in a film before cross-linking and a film at time *t*, respectively, the azide degradation rate constants (k_d) were obtained for each temperature studied (Figure 6). The data are linear, with the 222 °C data showing some

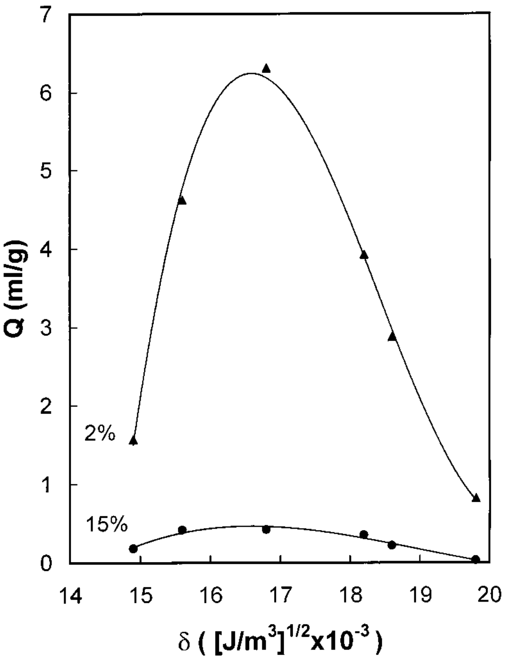


Figure 6. Loss of [N$_3$] in copolymer **6f** versus time at the indicated temperatures. The inset is an Arrhenius plot of the rates of thermal decomposition of the azide in the copolymer.

effects from a thermal lag in the heating system used for the cross-linking experiment. An Arrhenius plot of the resulting k_d values (inset to Figure 6) gave the activation energy for azide decomposition (E_a) in the copolymer. For copolymer **6f**, the activation energy was calculated to be 130 kJ/mol.

Swelling Measurements. Polymer films used for swelling experiments were cast from toluene solutions and were dried under vacuum at 50 °C. The conditions selected for cross-linking the copolymer films (250 °C, 3 h) were chosen to maximize the extent of cross-linking while minimizing thermal degradation. Thermal decomposition shows up as a visible yellowing of the samples and the appearance of new bands in the IR spectra at ~1700 cm^{-1}. Swelling measurements were performed on cross-linked copolymers that contained 2 mol % (**6a**) and 15 mol % azide (**6f**) before cross-linking. Pieces of the cross-linked copolymer films were cut and immersed in a series of poor H-bonding solvents[44] that are good solvents for PTMSP. After 24 h, the films were removed from the solvent, blotted dry, weighed, and returned to the solvent. After an additional 24 h, the procedure was repeated to ensure that the films had reached equilibrium. Figure 7 shows the results for these two cross-linked networks. Cross-linked copolymer **6a** swells significantly in octane, cyclohexane, and toluene, while cross-linked copolymer **6f** exhibits minimal swelling over the entire solvent range, with only a slight preference for octane, cyclohexane, and toluene. Cross-linked films of the entire series of azide copolymers (**6a**–**6g**) were placed into toluene (δ = 18.2 (J/m^3)$^{1/2}$ × 10^{-3}) and the degree of swelling measured. Figure 8 shows a dramatic decrease in swelling as the cross-linking density increases, with copolymers with azide contents greater than 5 mol % showing negligible swelling in toluene.

Discussion

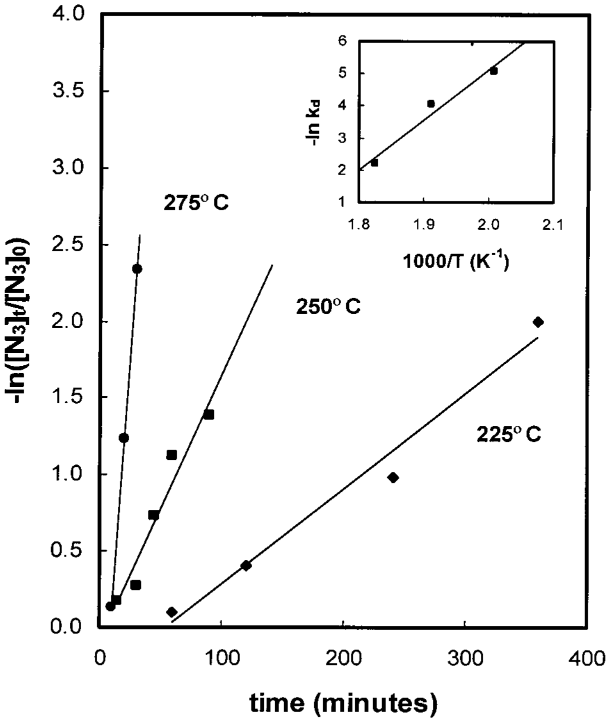


Figure 7. Swelling of thermally cross-linked films of copolymers **6a** and **6f** in solvents with different solubility parameters, δ ([J/m^3]$^{1/2}$ × 10^{-3}). Solvents: hexane (14.9), octane (15.6), cyclohexane (16.8), toluene (18.2), THF (18.6), CH$_2$Cl$_2$ (19.8).

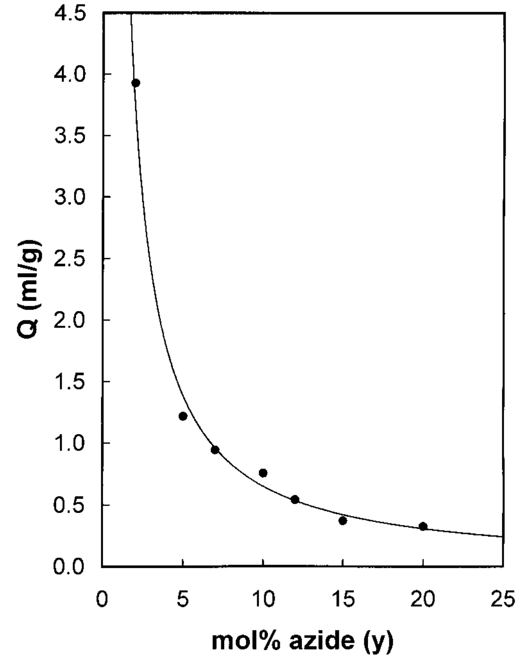


Figure 8. Swelling of thermally cross-linked films of copolymers **6a**–**6g** in toluene.

Synthetic Strategy. In a previous report, we explored the use of aryl azides as polymer cross-linking agents.[23] Cross-linkable PTMSP films were easily prepared by casting from polymer solutions containing added bis(aryl azide), but a major limitation of this scheme is that only low levels of aryl azide can be incorporated into most polymers before the onset of phase separation. In principle, the compatibility of aryl azides with polymer hosts could be improved through chemical modifications of the aryl azide structure. In similar fashion, alkyl azides could also be used in the form of an additive. The higher decomposition temperature of alkyl azides means that the processing window for polymers containing alkyl azides is wider than for those with aryl azides. One potential drawback, however, is that the higher temperatures needed for cross-linking might lead to some loss of the cross-linking agent from the polymer due to the volatility of the low molecular weight alkyl azide.

Our goal of reaching higher azide contents (and higher degrees of cross-linking) was achieved by directly attaching the azide group to the polymer backbone. In most polymers this would be an easy task since azides are good nucleophiles and can be introduced using simple S_N2 chemistry. However, the steric hindrance associated with the PTMSP backbone blocked our attempts to introduce the azide group. Copolymerization with a functional acetylenic comonomer followed by its conversion to the azide using a nucleophilic displacement reaction was necessary to incorporate larger amounts of azide functionality into PTMSP.

The addition of the tethered side chains does not appear to drastically alter the physical properties of the PTMSP backbone. The UV−vis absorption spectra of the copolymers are nearly identical to that of PTMSP. Neither PTMSP nor the copolymers strongly absorb above 280 nm, indicating that the C═C bonds are not conjugated and the rigid polymer backbone is retained. This conclusion is also supported by DSC data that indicate that the copolymers, like PTMSP, do not exhibit a glass transition below its thermal decomposition temperature.

The copolymerization route enabled us to overcome the problem of phase of separation at low azide contents and reach high degrees of cross-linking. While the highest azide content we explored in this work was 20 mol %, much higher levels are accessible by changing the monomer feed ratios during the synthesis of PTMSP copolymers.

Cross-Linking. Both aryl and alkyl azides can be activated using thermal or photochemical processes. The UV−vis spectra of PTMSP films containing bis(aryl azide) have two absorption maxima, one from PTMSP and a second from the bis(aryl azide) (e.g., 300 nm for 4,4′-diazidobenzophenone).[23] Because their absorption maximum occurs at lower energies, aryl azides can be photochemically decomposed selectively in optically clear substrates like PTMSP. Thus, the irradiation of PTMSP containing bis(aryl azide)s at 300 nm led to cross-linked films with no discernible damage to the host polymer. For alkyl azides, the absorption maximum is shifted to shorter wavelengths and coincides with the absorption band for PTMSP. Irradiation of the alkyl azide groups in poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] may lead to photochemistry that alters the structure of the polymer backbone. In addition, thick samples or those with high azide contents may be difficult to cure by UV.

DSC data show that polymers containing either alkyl or aryl azides thermally decompose, leading to cross-linked products. The limited compositional range available for aryl azide additives prevented us from examining the relationship between thermal decomposition and azide content in detail, but the data reported in this paper for alkyl azides indicate that the thermal properties show a linear dependence on composition over the entire range studied. Although the conditions required to cross-link alkyl azide substituted PTMSP are more severe than those required for the activation of bis(aryl azide)s, mechanically stable optically clear cross-linked networks with low levels of degradation were obtained. We also observed that copolymer films cast on glass exhibit excellent adhesive properties after cross-linking, either through chemical or physical interactions with the surface. Only after prolonged immersion in good solvents and sonication did a cross-linked film of copolymer **6f** fragment and dislodge from the glass surface.

The fate of the nitrenes formed during thermal or photochemical cross-linking is unknown. On the basis of the lack of reactivity of the double bond of PTMSP with electrophilic reagents such as bromine,[33] we believe that insertion reactions must be the dominant chemistry during cross-linking. To date, we have not seen clear physical evidence for insertion reactions due to the low azide contents in the polymers and the large number of potential sites for insertion.

Cross-linking the rigid polymer chains before they have a chance to interdiffuse results in stabilized low-density open structures with high amounts of free volume. Swelling measurements made on the series of cross-linked copolymer films (**6a**−**6g**) show that a low level of cross-linking yields materials impervious to solvent. Flexible polymers, such as polysiloxanes, typically require higher degrees of cross-linking to yield nonswelling films,[45] but the low levels of swelling observed in lightly cross-linked PTMSP networks could be anticipated from the known rigidity of the PTMSP chains. The slight swelling of PTMSP networks with greater than 10 mol % cross-linking, as measured by weight gain, is presumably due to solvent molecules occupying the free volume of the polymer. Compared to PTMSP membranes, the temporal stability of the cross-linked membranes is significantly improved. We observed no drop in the O_2 permeability of 5% cross-linked films over 1 month, while the permeability of PTMSP films dropped to 38% of its initial value during the same period. The details of the permeability and pervaporation properties of the series of copolymers will be reported elsewhere.

Comparison to Energetic Materials. Finally, we need to address the potential application of azide-containing PTMSP as an energetic material. For copolymer **6f**, an activation energy of 130 kJ/mol was calculated from IR data using the Arrhenius equation. This value compares well to the reported activation energy of another azide containing polymer, GAP, which has an $E_a = 120$ kJ/mol.[46] The copolymers are stable under ambient conditions and are not nearly as "shock sensitive" as trinitrotoluene (TNT) or nitroglycerine, which have activation energies of approximately 30 and 2 kJ/mol, respectively.[47]

The heat released during the thermal decomposition of azide in the copolymers is comparable to that other azide-based materials. The enthalpy of azide decomposition for the copolymer with the highest azide content in the series, **6g**, is −1.2 kJ/g, as measured by DSC. Two other azide-containing materials, GAP[6] and poly(vinyl nitrate) partially substituted with azide (PVAZ),[48] have reported enthalpies of −1.8 and −2.7 kJ/g, respectively. The higher enthalpies for these two polymers are due to the higher azide content incorporated in the structures. PTMSP with increased azide contents (>20 mol %) could easily be prepared by increasing the comonomer feed ratio or by homopolymerization of the functional comonomer. The molar enthalpies for thermal decomposition of copolymers **6a**−**6g** were also calculated from the DSC results. All copolymers in this series evolved approximately −800 kJ/mol N_3. This value is comparable to the measured molar decomposition enthalpy of a sample of PTMSP containing a known amount of nonvolatile dodecyl azide. Thus, the data indicate that the azide groups decompose independently, and the thermochemistry of the copolymers is additive.

Conclusions

Copolymers of 1-(4-azidobutyldimethylsilyl)-1-propyne and 1-trimethylsilyl-1-propyne were prepared by functionalizing the bromobutyl side chain of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-bromobutyldimethylsilyl)-1-propyne)] copolymers. The amount of N_3 in the copolymers was determined quantitatively by elemental analysis, DSC, and IR spectroscopy. Compared to the cross-linking of PTMSP by the physical addition of bis(aryl azide)s, copolymerization allowed incorporation of a higher concentration of cross-linking sites without phase separation. The measured activation energy and enthalpies of thermal decomposition of azide contained in the series of copolymers are comparable to other reported azide-containing materials. Thermally induced cross-linking of the copolymer films resulted in rigid, nonswelling materials at relatively low cross-link densities.

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References and Notes

(1) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297−368.
(2) Albini, A.; Bettinetti, G.; Minoli, G. *Heterocycles* **1993**, *35*, 885−893.
(3) Albini, A.; Bettinetti, G.; Minoli, G. *Heterocycles* **1995**, *40*, 597−605.
(4) Ger, M. D.; Hwu, W. H.; Huang, C. C. *Thermochim. Acta* **1993**, *224*, 127−140.
(5) Jones, D. E. G.; Malechaux, L.; Augsten, R. A. *Thermochim. Acta* **1994**, *242*, 187−194.
(6) Arisawa, H.; Brill, T. B. *Combust. Flame* **1998**, *112*, 533−544.
(7) Chang, T. C.; Wu, K. H.; Chen, H. B.; Ho, S. Y.; Chiu, Y. S. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 3337−3343.
(8) Kubota, N. *J. Propul. Power* **1995**, *11*, 677−682.
(9) Shanthi, C.; Rao, K. P. *J. Biomater. Sci., Polym. Ed.* **1997**, *8*, 919−930.
(10) van der Heiden, A. P.; Willems, G. M.; Lindhout, T.; Pijpers, A. P.; Koole, L. H. *J. Biomed. Mater. Res.* **1998**, *40*, 195−203.
(11) Kuijpens, J. M. H.; Kardaun, G. A.; Blezer, R.; Pijpers, A. P.; Koole, L. H. *J. Am. Chem. Soc.* **1995**, *117*, 8691−8697.
(12) Aldenhoff, Y. B. J.; Koole, L. H. *J. Biomed. Mater. Res.* **1995**, *29*, 917−928.
(13) Vilven, J. C.; Domalewski, M.; Prossnitz, E. R.; Ye, R. D.; Muthukumaraswamy, N.; Harris, R. B.; Freer, R. J.; Sklar, L. A. *J. Recept. Signal Transduct. Res.* **1998**, *18*, 187−221.
(14) Tate, J. J.; Persinger, J.; Bartholomew, B. *Nucleic Acids Res.* **1998**, *26*, 1421−1426.
(15) Lavrik, O. I.; Nasheuer, H. P.; Weisshart, K.; Wold, M. S.; Prasad, R.; Beard, W. A.; Wilson, S. H.; Favre, A. *Nucleic Acids Res.* **1998**, *26*, 602−607.
(16) Hanna, M. M.; Zhang, Y. Y.; Reidling, J. C.; Thomas, M. J.; Jou, J. *Nucleic Acids Res.* **1993**, *21*, 2073−2079.
(17) Morita, H.; Mori, S.; Uchino, N.; Yokoyama, S. *Z. Phys. Chem., Int. J. Res. Phys. Chem. Chem. Phys.* **1993**, *182*, 209−216.
(18) Murray, K. A.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1996**, *76*, 161−163.
(19) Gonzalez, L.; Rodriguez, A.; deBenito, J. L.; MarcosFernandez, A. *J. Appl. Polym. Sci.* **1997**, *63*, 1353−1359.
(20) Yan, M. D.; Cai, S. X.; Wybourne, M. N.; Keana, J. F. W. *J. Mater. Chem.* **1996**, *6*, 1249−1252.
(21) Naito, I.; Morihara, H. *J. Imaging Sci. Technol.* **1996**, *40*, 50−55.
(22) Yamamoto, J.; Uchino, S.; Hattori, T.; Yoshimura, T.; Murai, F. *Jpn. J. Appl. Phys., Part 1: Regul. Pap. Short Notes Rev. Pap.* **1996**, *35*, 6511−6516.
(23) Jia, J. P.; Baker, G. L. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 959−968.
(24) Abramovitch, R. A.; Kyba, E. P. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Interscience Publishers: London, 1971; pp 221−330.
(25) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473.
(26) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M.; Masuda, T.; Higashimura, T. *Kobunshi Ronbunshu* **1986**, *43*, 747.
(27) Masuda, T.; Higashimura, T. In *Silicon Based Polymer Science*; Ziegler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series Vol. 224; American Chemical Society: Washington, DC, 1990; p 641.
(28) Nagai, K.; Higuchi, A.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 289−298.
(29) Nagai, K.; Nakagawa, T. *J. Membr. Sci.* **1995**, *105*, 261−272.
(30) Masuda, T.; Isobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 841.
(31) Baker, G. L.; Klausner, C. F.; Gozdz, A. S.; Shelburne, J. A.; Bowmer, T. N. *Adv. Chem. Ser.* **1990**, *224*, 663−678.
(32) Kraus, G.; Landgrebe, K. *Synthesis* **1984**, *10*, 885.
(33) Kunzler, J.; Percec, V. *New Polym. Mater.* **1990**, *1*, 271.
(34) Bowmer, T. N.; Baker, G. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 218.
(35) Nishiyama, K.; Karigomi, H. *Chem. Lett.* **1982**, *9*, 1477.
(36) Gilbert, E. E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3603.
(37) Hidalgo, M.; Gonzalez, L.; Mijangos, C. *J. Appl. Polym. Sci.* **1996**, *61*, 1251−1257.
(38) Jayakrishnan, A.; Sunny, M. C.; Rajan, M. N. *J. Appl. Polym. Sci.* **1995**, *56*, 1187−1195.
(39) Cohen, H. L. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1337−1347.
(40) Ravindranath, B.; Srinivas, P. *Ind. J. Chem.* **1985**, *24B*, 1178.
(41) Gurst, J. E. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Interscience Publishers: London, 1971; pp 191−202.
(42) Gozdz, A. S.; Baker, G. L.; Klausner, C.; Bowden, M. J. *Proc. SPIE* **1987**, *771*, 18.
(43) Tang, B. Z.; Masuda, T.; Higashimura, T.; Yamaoka, H. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 1197−1209.
(44) Burrell, H. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1975; p IV-337.
(45) Pleshakov, D. V.; Lotmentsev, Y. M. *Vysokomol. Soedin.* **1994**, *36*, 2026−2030.
(46) Eroglu, M. S. *Polym. Bull.* **1998**, *41*, 69−76.
(47) Johansson, C. H.; Persson, P. A. *Detonics of High Explosives*, 1st ed.; Academic Press: New York, 1970.
(48) Mishra, S. C.; Pant, J.; Dutta, P. K.; Durgapal, U. C. *Def. Sci. J.* **1997**, *47*, 131−137.

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